MEASUREMENTS OF NO_3 AND IO DURING ACSOE

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• Introduction: The technique of *D*ifferential *O*ptical *A*bsorption *S*pectroscopy (DOAS) was used to determine the concentrations of NO_3 and IO during a number of field experiments carried out at Mace Head on the West coast of Ireland, and on the island of Tenerife. Both species play an important role in the oxidising capacity of the troposphere: NO_3 dominates the night-time troposphere acting as an oxidising agent for a number of NMHCs and also providing a route for the removal of NO_x via the non-photochemical conversion of NO_x to nitric acid; Iodine is thought to have a number of important roles in atmospheric chemistry which include its potential role as a catalyst for tropospheric O_3 destruction via reactions of IO, and also the removal of NO_x from the gas phase through the recombination of NO_2 with IO and subsequent aerosol uptake. Figures 1 and 2 show a simplified reaction scheme for both NO_3 and iodine, respectively.

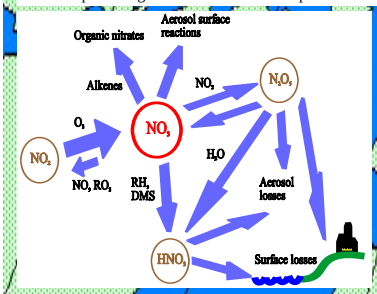


Figure 1: A simplified NO_3 reaction scheme.

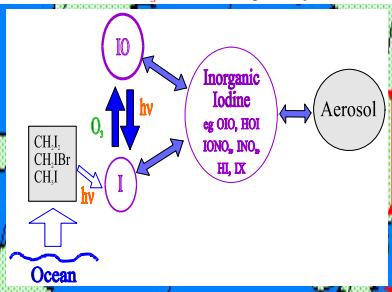
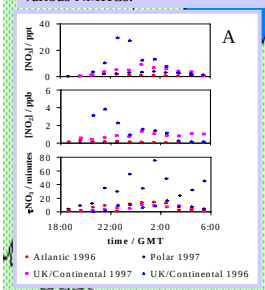


Figure 2: A simplified Iodine reaction scheme.

• Boundary Layer NO_3: The observations of boundary layer (BL) NO_3 are summarised below. Figure 3 shows typical profiles for the NO_3 and NO_2 concentration and NO_3 lifetime (τNO_3) determined for each type of airmass experienced at each location during the campaigns (the airmass classification for each site can be seen on the background to this poster). In the clean Atlantic air observed at both sites the 24 hour mean [NO_3] ranged from 1.3-9.1x10^7 molecule cm^{-3}. When compared to the 24 hour OH average of 7x10^5 molecule cm^{-3} [D.J. Creasey, pers. comm.], shows that the oxidising capacity of NO_3 is comparable to that of OH for DMS and various NMHCs.



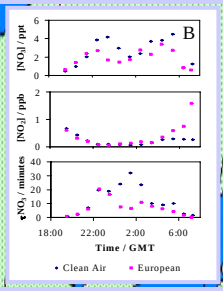


Figure 3: The median value of NO_3, NO_2 and τNO_3 plotted with the 25 and 75 percentiles for each sector at Mace Head (A) and Tenerife (B).

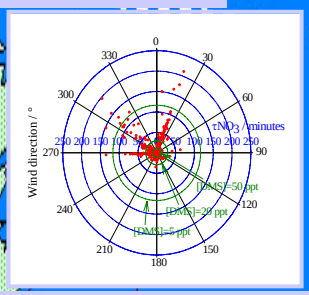


Figure 4: A polar plot showing the observed τNO_3 versus wind direction. The green circles represent the calculated lifetime of NO_3 assuming that 5, 20 and 50 ppt of DMS were present.

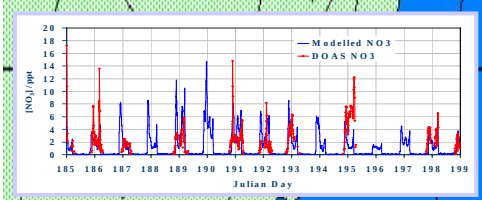
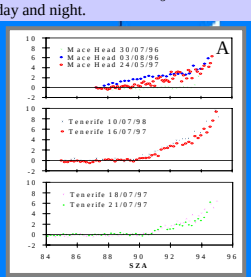


Figure 5: Modelled and observed NO_3 for the campaign based on Tenerife during July 1997.

The reaction of DMS with NO_3 can act as a major loss of NO_3 in the marine boundary layer (MBL). Although high levels of DMS are expected in the MBL during summer months this was not the case for Mace Head and this is reflected in τNO_3 shown in figure 4. From the modelling studies carried out on the data obtained on Tenerife (Figure 5), however, it was found that the major loss mechanism was DMS where levels of DMS varied between 50-80 ppt. By modelling a wide variety of conditions in the MBL it was found that when $[NO_x]>0.6[DMS]$, DMS will be oxidised more rapidly at night by NO_3 than during the day by OH. Model studies also show that in conditions where $[NO_x]<1$ ppb and DMS dominates the NO_3 chemistry the rate of formation of HNO_3 (a major sink of NO_x) is comparable during both day and night.

• Free Tropospheric NO_3: The change in the vertical column of NO_3 observed during sunrise arises from increasing amounts of NO_3 being photolysed as the solar terminator sweeps down through the atmosphere. Therefore, in principle, the change in the NO_3 total column with the change in terminator height can be used to infer a vertical concentration profile of NO_3. Figures 6 and 7 summarise some observations of NO_3 throughout the troposphere during sunrise at Mace Head and Tenerife.



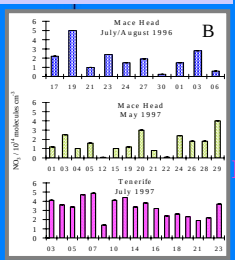


Figure 6: Observed column abundance of NO_3 during sunrise. A - shows the decrease in NO_3 measured; B - shows the total tropospheric column of NO_3 calculated at 93° SZA.

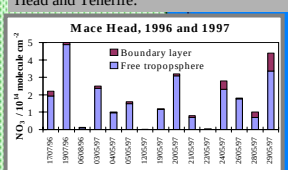


Figure 7: The contribution to the total column to NO_3 at 93° from the BL (assuming 1 km, well mixed BL) and free troposphere.

• Boundary Layer IO: These data are amongst the first observations of IO in the MBL. The data from Tenerife are the first measurements of IO at an open ocean location. On all days at Tenerife the air mass being sampled had travelled for at least 3 days from the north/ north-west Atlantic. A clear diurnal cycle in the IO profile is observed (peaking around midday at 1-4 ppt) which is expected as the major source of atmospheric iodine is believed to be the photochemical degradation of organic iodine-containing molecules produced biogenically in the upper ocean. Modelling studies indicate that iodine-catalysed O_3 destruction ranged from 4 to 13 % per day at these levels of IO, similar to the loss caused by odd-hydrogen photochemistry and dry deposition.

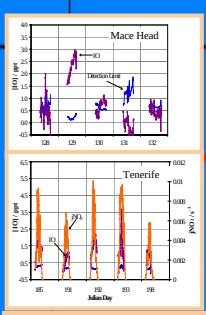


Figure 8: Observed IO profiles. Note the correlation between the IO and photolysis of NO_2 (jNO_2).

•Acknowledgements

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